Magnetite-rutile symplectite in ilmenite records magma hydration in layered intrusions

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ABSTRACT

The textures and geochemical characteristics of the rocks in layered intrusions potentially provide insights into the physicochemical processes that have taken place in mafic magma chambers. Diverse exsolution textures of Fe-Ti oxides in layered intrusions may record the variation of subsolidus temperature and oxygen fugacity ($f_\text{O}_2$) of cooling magma chambers. Here we investigated ilmenite-hematite solid solution (Ilm$_\text{ss}$) relationships evident in preserved intergrowths of magnetite-rutile and ilmenite-hematite in the gabbro of the Xinjie layered intrusion. The crystallographic orientation and 3D morphology of the two intergrowth types constrain the transformation mechanism of the exsolution textures from Ilm$_\text{ss}$. The results reveal that the interface of the ilmenite-hematite intergrowth is more energetically favorable than that of the magnetite-rutile symplectite when they are transformed from Ilm$_\text{ss}$ on cooling. The QUILF equilibria suggests that the magnetite-rutile symplectite can be transformed from Ti-rich ilmenite with Ilm$_{0.95}$ above 550 °C when the subsolidus $f_\text{O}_2$ trend is buffered by the biotite-ilmenite-feldspar-ulvöspinel (KUIlB) mineral assemblages crystallized from hydrated mafic magmas. The magnetite-rutile symplectite may be used as a unique texture indicator of magma hydration in the evolution history of terrestrial, martian, and lunar magmas.

Keywords: Magnetite-rutile symplectite, ilmenite-hematite solid solution (Ilm$_\text{ss}$), magma hydration, layered intrusion

INTRODUCTION

Layered intrusions preserve the fully crystalline products of magmas that may have experienced different physicochemical processes in mafic magma chambers (e.g., Holness et al. 2017 and references therein). One fundamental aspect of the petrogenesis of layered intrusions that remains controversial is the link between rock textures and magmatic processes (McBirney and Hunter 1995; Latypov et al. 2018; Kruger and Latypov 2020). Despite intense studies in this area, studies concerning the exsolution textures in minerals and the subsolidus evolution of layered intrusions have been rarely reported (Buddington and Lindsley 1964; McConnell 1975). The diverse exsolution textures of Fe-Ti oxides in the rocks of layered intrusions have been suggested to record the variation of temperature and oxygen fugacity ($f_\text{O}_2$) of the magma chamber during crystallization and subsolidus cooling (Haggerty 1991; Frost 1991; Lattard et al. 2005; Brownlee et al. 2010). Understanding the transformation mechanism of these exsolution textures is critical to constrain the subsolidus cooling processes of layered intrusions.

The ilmenite-hematite (FeTiO$_3$-Fe$_2$O$_3$) solid solution (Ilm$_\text{ss}$) commonly occurs in layered intrusions (Harrison et al. 2000). Ilm$_\text{ss}$ tends to experience subsolidus re-equilibration and phase transformation during different $f_\text{O}_2$ cooling paths, forming hematite and/or magnetite exsolution and magnetite-rutile intergrowths in ilmenite (Robinson et al. 2002; Tan et al. 2015, 2016; Guo et al. 2017). Experimental results indicate that intergrowths of magnetite-rutile and ilmenite-hematite, which are transformed from Ilm$_\text{ss}$, are thermodynamically equivalent over a large temperature interval (Lindsley 1991). However, the magnetite-rutile intergrowth is rare in natural rocks relative to the ilmenite-hematite intergrowth. The interfacial properties of different phases are considered to be critical to the subsolidus transformation processes (Feinberg et al. 2004; Hammer et al. 2010; Wenk et al. 2011; De Yoreo et al. 2015; Xu et al. 2015; Xu and Wu 2017) and may serve to solve this paradox. However, the orientation relationships of Fe-Ti oxides have not yet been investigated, so the effect of interfacial properties of different phases has not been fully understood. The formation of the ilmenite-hematite intergrowth is usually ascribed to the decomposition of Ilm$_\text{ss}$ when the temperature falls below that of the solvus (Harrison et al. 2000). In contrast, the magnetite-rutile intergrowth is likely related to fluids in layered intrusions and metamorphic rocks (Southwick 1968; Tan et al. 2015; Guo et al. 2017). However, there is no direct textual evidence for the oxidation of Ilm$_\text{ss}$ reported so far. Moreover, it remains enigmatic what controls the oxidizing $f_\text{O}_2$ trends of the mafic magmas from which the layered intrusions formed.

The $f_\text{O}_2$ fluctuation and interfacial properties of the intergrowths have been proposed to be potential factors affecting the
subsolidus transformation of IIm$_{ss}$ (Lindsley 1991). However, it remains unclear how different intergrowths are developed during the transformation of IIm$_{ss}$. In this study, we report both magnetite-rutile symplectite and ilmenite-hematite intergrowth that are transformed from the same IIm$_{ss}$ precursor in the Xinjie layered intrusion, southwest (SW) China, and examine the interfacial properties of the two intergrowths and the transformation mechanisms involved. We use electron backscatter diffraction (EBSD) and focused ion beam–energy-dispersive X-ray spectroscopy (FIB-EDS) tomography to investigate the crystallographic orientation, 3D morphology and texture of the two intergrowths. We also use the compositions of the Fe-Ti oxides to constrain the formation temperature ($T$) and $f$O$_2$ of different intergrowths in the QUILF equilibria (Andersen et al. 1993). This study sheds light on the coherence between diverse exsolution textures of IIm$_{ss}$ and subsolidus $T$-$f$O$_2$ trends in a cooling mafic magmatic system. As ilmenite is also ubiquitous in the lunar and martian magmatic rocks (Raymond and Wenk 1971; Wang et al. 2004; Santos et al. 2015), the results in this study can be helpful to the understanding of physicochemical conditions of magmatic processes on the Moon and Mars.

### ANALYTICAL METHODS

**Electron backscatter diffraction**

Thin sections from the analyzed samples were polished with 0.05 µm colloidal silica for 3 h to allow EBSD analysis, SEM imaging and EBSD analysis were conducted on a Tescan MIRA3 Field Emission SEM, housed in the Microscopy & Microanalysis Facility (John de Laeter Centre) at Curtin University, Perth, Western Australia, and on a FEI Quanta 450 field emission gun SEM housed in the State Key Laboratory and Geological Process and Mineral Resources (GPMR) of China University of Geosciences (Wuhan). The EBSD measurement was performed with an accelerating voltage of 20 kV and a working distance of ~20 mm. Electron backscatter patterns (EBSPs) were automatically collected and indexed over a regular grid with a 290 nm step size by using the Oxford Aztec 4.1 software. The CHANNEL 5+ software was used for plotting color-coded maps and the low hemisphere equal area pole figures of the indexed mineral. Noise reduction was performed by using a “wildspike” correction and a five-neighbor zero solution extrapolation.

**3D FIB-EDS tomography**

The 3D tomography was performed using a Helios G4 Dual Beam Workstation at the Thermo-Fisher Scientific Inc., Shanghai. A selected volume was extracted from the area of interest using the focused Ga-ion beam (acceleration voltage 30 kV) for 3D reconstruction. The chemical analyses of Fe, Ti, and O were carried out using acceleration voltage 8 kV and beam current 13 nA. The energy-dispersive X-ray spectroscopy (EDS) analysis was performed in mapping mode to investigate the two-dimensional distributions of Fe, Ti, and O. Serial cross-section slices were produced by cutting the selected volume using focused Ga-ion beam, with a distance of 50 nm between slices, and an EDS mapping was collected for every three milling steps. The scripting routine was performed automatically with the “Auto slice and view 5.0” software. After data collection, the 2D image sequences were aligned, cropped, and stacked into a 3D microstructure image. A total 3D volume of $31.6 \times 11.8 \times 13.25 \mu$m$^3$ with a voxel pixel of $11.53 \times 11.53 \times 50 \text{nm}^3$ was reconstructed for further analysis.

### RESULTS

**Major petrographic features of the Xinjie layered intrusion**

The Xinjie intrusion is one of several layered intrusions in the Panzhihua-Xichang region in SW China (Fig. 1a). The intrusion is a northwest-southeast striking, sill-like body approximately 7.5 km long, 1–1.5 km wide, and 1.2 km thick, and is divided from the base upward into a marginal zone and three lithological cycles (Units I, II, and III) (after Wang et al. 2008). Units I and II contain different modal proportions of olivine, clinopyroxene, plagioclase, and Fe-Ti oxides, forming interlayered wehrlite, olivine gabbro, olivine clinopyroxenite, clinopyroxenite, and melagabbro (Fig. 1b). Wehrlite and olivine clinopyroxenite in Units I and II display similar texture, and contain <10 vol% cumulus and intercumulus Fe-Ti oxides that are scattered in the rocks (Figs. 2a and 2b). Hydrous silicates (e.g., amphibole and biotite) are scarce in Units I and II. Unit III is mainly composed of gabbro with < 30 vol% Fe-Ti oxides (Figs. 2c and 2d), but it hosts two thick (40–50 m thick) and one thin (~4 m thick) oxide gabbro layers that contain ~0–70 vol% Fe-Ti oxides (Fig. 1b).
The rocks of Unit III generally contain 2–5 vol% hydrous silicates, which are locally gathered and closely associated with Fe-Ti oxides (Fig. 2d).

The exsolution textures in both cumulus and intercumulus ilmenite can be divided into three types, which are distributed unevenly along the profile throughout the intrusion (Fig. 1b). The ilmenite in Units I and II is generally homogeneous in BSE images and only displays local hematite lamellae (type-I, Figs. 3a and 3b). The ilmenite in Unit III commonly contains symplectitic intergrowth of magnetite-rutile (type-II, Fig. 3c) and is closely associated with hydrous silicates (Figs. 3d and 3e). Both type-I and type-II intergrowths are observed in the ilmenite of the melagabbro at the bottom of Unit III, which was then selected to investigate in this study. In addition, the ilmenite in the Fe-Ti oxide gabbro layer of Unit III contains magnetite exsolution (type-III, Fig. 3f).

**Appearance of magnetite-rutile symplectite and ilmenite-hematite intergrowth**

Magnetite-rutile symplectites in ilmenite comprise micro- to nano-scale anhedral magnetite and rutile (Fig. 4a). The dendritic rutile tends to pinch outward and is truncated by magnetite (Fig. 4b). The symplectites have discrete and irregular boundaries with the host ilmenite (Fig. 4c). Nanoscale hematite is evenly distributed (Fig. 4d) and oriented parallel to the (0001) planes of the host ilmenite.

Most rutile grains are enveloped by continuous magnetite and show dendritic shapes in the 3D images (Fig. 5a and Online Materials1 movie OM1). The dendritic rutile appears isolated in the 2D backscattered electron (BSE) images but is actually interconnected in the 3D morphology (Fig. 5b and Online Materials1 movie OM2). Magnetite appears as a connected matrix in the symplectite (Fig. 5c and Online Materials1 movie OM2).
Figure 3. BSE images of ilmenite grains hosting different types of exsolution textures in the Xinjie intrusion. (a) Euhedral ilmenite as inclusions in silicates showing no exsolution (type-I) in Unit I. (b) Elongated ilmenite showing well-oriented hematite lamellae (type-I) in Unit II. (c) Occurrence of magnetite-rutile symplectite (type-II) in ilmenite grain from the leucogabbro in Unit III. (d) Biotite coexisting with plagioclase and ilmenite hosting magnetite-rutile symplectite (type-II) from the olivine gabbro at the bottom of Unit III. (e) Amphibole coexisting with plagioclase, titanomagnetite, and ilmenite hosting magnetite-rutile symplectite (Type-II) from the olivine gabbro at the bottom of Unit III, note the skeletal titanomagnetite (left) formed by subsolidus reaction. (f) Occurrences of magnetite (type-III) in different ilmenite grains coexisted with cumulus titanomagnetite in the Fe-Ti oxide gabbro at the bottom of Unit III. Ilm = ilmenite; Hem = hematite; Tmt = titanomagnetite; Sym = symplectite; Mag = magnetite.
Massive lens-like hematite lamellae have sharp contacts with the host ilmenite, forming ilmenite-hematite intergrowth (Fig. 5d).

**Compositions of magnetite-rutile symplectite and ilmenite-hematite intergrowth**

The EMPA results indicate that rutile in the magnetite-rutile symplectite contains 95.97 to 98.63 wt% TiO$_2$ and 1.38 to 3.59 wt% FeO. Magnetite in the symplectite contains 33.58 to 35.63 wt% FeO, 59.50 to 63.70 wt% Fe$_2$O$_3$, and 2.72 to 4.68 wt% TiO$_2$ (Table 1). The mineral mode of rutile in the symplectite is ~40 wt% (~45 vol%), and magnetite is ~60 wt% (~55 vol%) so that the symplectite is estimated to contain 21.90 wt% FeO, 36.82 wt% Fe$_2$O$_3$, and ~41.19 wt% TiO$_2$ in bulk composition (Table 1).

The ilmenite-hematite intergrowth contains 41.39–43.05 wt% FeO, 47.40–49.50 wt% TiO$_2$, and 6.76–10.94 wt% Fe$_2$O$_3$ in bulk composition (Table 2). Given that the hematite lamellae mainly contain Fe and O based on the scanning transmission electron mode with energy-dispersive spectrometer (STEM-EDS) mapping (Online Materials1 Fig. OM1), the variation of Fe$_2$O$_3$ is likely related to the uneven distribution of nano-scaled hematite lamellae in the intergrowth.

**Crystallographic orientation of minerals**

The host ilmenite exhibits consistent crystallographic orientation (Figs. 6a and 6e). The majority of magnetite in the symplectite shares a common {111}$_{Mag}$ plane and a set of corresponding <110>$_{Mag}$ directions on the common {111}$_{Mag}$ plane. In detail, there is an angular variation of ~4.5° across the magnetite (Fig. 6b). Similarly, the majority of rutile shares a common {100}$_{Rt}$ plane and corresponding in-plane <001>$_{Rt}$ + <011>$_{Rt}$ directions with an angular variation of ~16° (Fig. 6c). The lattice orientations of a single rutile and magnetite grain record the progressive variation of up to ~1.6 and ~3, respectively (Fig. 6d). Note that the shared {100}$_{Rt}$ and {111}$_{Mag}$ planes fall into the same area as the (0001)$_{Ilm}$ plane, and the shared <001>$_{Rt}$ and <011>$_{Rt}$ directions and <110>$_{Mag}$ directions also fall into the same area as the <1010>$_{Ilm}$ directions (Figs. 6e–g). It is likely that the crystallographic orientations of the majority of magnetite and rutile are controlled by the host ilmenite. Therefore, there is an orientation relationship among the magnetite-rutile symplectites and the host ilmenite, such that {100}$_{Rt}$/ {111}$_{Mag}$/ (0001)$_{Ilm}$ and (<011>$_{Rt}$ + <001>$_{Rt}$)/<110>$_{Mag}$/<1010>$_{Ilm}$.

The crystallographic projections of both the host ilmenite and hematite lamellae are parallel to each other along the (0001)
plane (Robinson et al. 2002). The lattice fringes at the ilmenite-hematite interface run straightly across all the directions on the high-resolution transmission electron microscopy (HRTEM) images (Online Materials Fig. OM2).

**DISCUSSION**

**Thermo-dynamic factors controlling the subsolidus transformation of Ilm**

Ilmenite-hematite intergrowths are commonly interpreted as a subsolidus transformation product of Ilm (Robinson et al. 2002). The HRTEM images reveal that the ilmenite and hematite have the same crystallographic orientation and form highly coherent interfaces in the intergrowth (Online Materials Fig. OM2), which can be attributed to their crystallographic similarity (Robinson et al. 2002). The irregular morphologies of magnetite and rutile indicate that the two minerals crystallized concurrently. In addition, the orientation relationships between the magnetite, rutile, and host ilmenite indicate that their orientations are inherited from the Ilm precursor (Figs. 6e–g). Thus, the ilmenite-hematite intergrowth and the magnetite-rutile symplectite represent two types of transformation products of an Ilm precursor.

In general, the Fe-Ti oxides have distinctly different close-packed frameworks for their oxygen atoms; hematite, ilmenite, and rutile have “hexagonal close packing” frameworks, whereas magnetite has a “cubic close packing” framework. Hematite and ilmenite have oxygen atoms closely packed or nearly close-packed on the basal (0001) plane and along the <1010> direction (Figs. 7a and 7b). Magnetite has oxygen atoms packed on the {111}Mag and along the <110>Mag (Fig. 7c). Rutile has

**Table 1. Major oxide compositions of rutile and magnetite in the magnetite-rutile symplectite (in wt%)**

<table>
<thead>
<tr>
<th>Major oxides</th>
<th>Rutile</th>
<th>Magnetite</th>
<th>Bulk composition^a</th>
<th>(in average)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 3 4 5 6</td>
<td>1 2 3 4 5 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.02 0.01 0.02 0.00 0.01 0.02</td>
<td>0.02 0.01 0.00 0.00 0.27 0.01 0.00</td>
<td>0.03 (0)</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.01 0.02 0.01 0.04 0.03 0.03</td>
<td>0.05 0.02 0.00 0.00 0.00 0.00 0.00 0.01</td>
<td>0.02 (0)</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.00 0.01 0.02 0.02 0.02 0.02</td>
<td>0.00 0.01 0.01 0.00 0.04 0.01 0.00</td>
<td>0.01 (0)</td>
<td></td>
</tr>
<tr>
<td>FeO*</td>
<td>2.43 2.91 1.38 2.63 3.59 2.87</td>
<td>34.91 33.58 34.01 35.06 34.85 35.63 35.12</td>
<td>22.14 (0.69)</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃*</td>
<td>– – – – – –</td>
<td>59.50 63.70 62.15 61.68 61.41 60.42 60.68</td>
<td>37.28 (1.33)</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.02 0.01 0.00 0.00 0.00 0.00</td>
<td>0.04 0.01 0.00 0.00 0.00 0.00 0.01 0.02</td>
<td>0.01 (0)</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>0.00 0.00 0.00 0.00 0.00 0.00</td>
<td>0.08 0.09 0.09 0.01 0.07 0.05 0.05</td>
<td>0.04 (0)</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.00 0.00 0.00 0.03 0.03 0.00</td>
<td>0.02 0.03 0.02 0.03 0.02 0.01 0.00</td>
<td>0.01 (0)</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>97.77 96.63 96.83 97.29 95.97 96.43</td>
<td>4.50 2.72 3.36 4.06 3.64 4.68 4.34</td>
<td>40.48 (2.02)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.24 99.59 100.03 100.01 99.64 99.36</td>
<td>99.11 100.16 99.64 100.84 100.30 100.81 100.21</td>
<td>100.02 (0.01)</td>
<td></td>
</tr>
</tbody>
</table>

Notes: Redistribution of the measured 2FeO between Fe₂O₃* and FeO* is on the basis of charge balance and stoichiometry of magnetite. *The average bulk composition of the rutile-magnetite symplectite is based on the modal proportion analysis of rutile/magnetite ratios on BSE images, rutile takes up ~45 vol% (~40 wt%) and magnetite ~55 vol% (~60 wt%) in average. Standard deviations are listed in the parentheses.

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Figure 6. Microstructure and orientation for the major phases in the magnetite-rutile symplectite and host ilmenite constructed from EBSD data. (a) Phase-color map of magnetite (Mag, green), rutile (Rt, fuchsia) and host ilmenite (Ilm). (b) Magnetite lattice orientation variations to 4.5° from the red cross (TC_Mag, texture component for magnetite). (c) Rutile lattice orientation variations to 16° from the red cross (TC_Rt, texture component for rutile). (d) Grain reference orientation deviation angle (GROD angle) showing the deviation angle from the average orientation of a rutile grain and its surrounding magnetite. (e–g) Lower hemisphere equal area projection patterns of host ilmenite, magnetite matrix, and vermicular rutile, colored with their phase colors in (a). The circles and triangles indicate the parallel planes and directions of different minerals, respectively. Note: the data on each model indicate the periodic distance of every four oxygen atoms along \( <10\overline{1}0>_{\text{Ilm}} \), \( <10\overline{1}0>_{\text{Hem}} \), \( <110>_{\text{Mag}} \), and \( <011>_{\text{Rt}} + <001>_{\text{Rt}} \), respectively.

**Table 2.** Bulk major oxide compositions of ilmenite-hematite intergrowth (in wt%)

<table>
<thead>
<tr>
<th>Major oxides</th>
<th>Major oxides 1</th>
<th>Major oxides 2</th>
<th>Major oxides 3</th>
<th>Major oxides 4</th>
<th>Major oxides 5</th>
<th>Major oxides 6</th>
<th>Major oxides 7</th>
<th>Major oxides 8</th>
<th>Major oxides 9</th>
<th>Major oxides 10</th>
<th>Average</th>
<th>Bulk composition including two intergrowths</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01 (0.01)</td>
<td>0.02 (0)</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.33</td>
<td>0.34</td>
<td>0.35</td>
<td>0.35</td>
<td>0.33</td>
<td>0.35</td>
<td>0.34</td>
<td>0.33</td>
<td>0.32</td>
<td>0.34 (0.01)</td>
<td>0.16 (0.03)</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00 (0)</td>
<td>0.01 (0)</td>
<td></td>
</tr>
<tr>
<td>FeO(^*)</td>
<td>42.06</td>
<td>43.03</td>
<td>42.77</td>
<td>42.90</td>
<td>42.31</td>
<td>43.24</td>
<td>42.32</td>
<td>41.39</td>
<td>41.75</td>
<td>42.54 (0.63)</td>
<td>39.55 (0.64)</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3)*</td>
<td>9.42</td>
<td>7.54</td>
<td>8.14</td>
<td>7.86</td>
<td>8.93</td>
<td>6.76</td>
<td>8.56</td>
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<td>10.66</td>
<td>7.59</td>
<td>8.45 (1.32)</td>
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<tr>
<td>MnO</td>
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<td>0.65</td>
<td>0.74</td>
<td>0.66</td>
<td>0.71</td>
<td>0.67</td>
<td>0.65</td>
<td>0.66</td>
<td>0.61</td>
<td>0.65</td>
<td>0.67 (0.02)</td>
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</tr>
<tr>
<td>NiO</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.05</td>
<td>0.00</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
<td>0.02 (0.02)</td>
<td></td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.03</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>0.03</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01 (0.01)</td>
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</tr>
<tr>
<td>TiO(_2)</td>
<td>48.17</td>
<td>49.25</td>
<td>49.08</td>
<td>49.12</td>
<td>48.52</td>
<td>49.50</td>
<td>48.45</td>
<td>47.40</td>
<td>47.75</td>
<td>49.22</td>
<td>48.70 (0.70)</td>
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<tr>
<td>Total</td>
<td>100.70</td>
<td>100.83</td>
<td>101.08</td>
<td>100.97</td>
<td>100.86</td>
<td>100.55</td>
<td>100.35</td>
<td>100.78</td>
<td>101.14</td>
<td>100.83</td>
<td>100.73 (0.01)</td>
<td></td>
</tr>
</tbody>
</table>

Notes: Redistribution of the measured \( \Sigma \text{FeO} \) between FeO\(^*\) and FeO\(^*\) is on the basis of charge balance and stoichiometry of ilmenite. The bulk composition including the ilmenite-hematite intergrowth and the rutile-magnetite symplectite. The modal proportions of symplectite in different ilmenite grains range from 34 to 58%, and the resulted standard deviations of the bulk composition are listed in the parentheses. \( X_{\text{Ilm}} \) and \( X_{\text{Hem}} \) refer to mole fractions of ilmenite and hematite, respectively. Standard deviations are listed in the parentheses.
In this case, the $\Delta G_f$ can be estimated by the lattice misfit of the oxygen atom framework ($\delta$) at their interfaces (Feinberg et al. 2004; Wenk et al. 2011).

The lattice misfit of the oxygen atom framework along the interface of hematite and ilmenite can be estimated using the oxygen atomic spacing of two minerals, i.e., $\delta_{\text{Ilm-Hem}} = (a_{\text{Ilm}} - a_{\text{Hem}})/a_{\text{Hem}}$ where $a_{\text{Ilm}}$ and $a_{\text{Hem}}$ refers to the oxygen atomic spacing of ilmenite and hematite, respectively. The $\delta_{\text{Ilm-Hem}}$ is then estimated to be $\sim 1\%$ (Figs. 7a and 7b). Likewise, the lattice misfit of the oxygen framework along the magnetite-rutile interface ($\delta_{\text{Mag-Mag}}$) is estimated to be $\sim -9.8\%$ (Figs. 7c and 7d). The relatively high $\delta_{\text{Ilm-Hem}}$ value makes the formation of ilmenite-hematite intergrowth energetically favorable when the temperature falls below the solvus of Ilm$_a$ on subsolidus cooling, in accordance with its high frequency in natural occurrence.

**Transformation of magnetite-rutile symplectite from Ilm$_a$ precursor**

The textural relationship shown in 3D images indicates that the dendritic rutile in the magnetite-rutile symplectite is likely the first phase exsolved from the Ilm$_a$, and predated the matrix magnetite (Figs. 5b and 5c). The bulk composition of the symplectite is reconstructed to have $\sim 37\%$ Fe$_2$O$_3$ (Table 1), much higher than that for coexisting ilmenite-hematite intergrowth ($\sim 8.5\%$ Fe$_2$O$_3$, Table 2), indicating that the formation of the symplectite is related to the oxidation state rather than the isochemical decomposition of the Ilm$_a$ precursor. The exsolution of rutile is ascribed to the subsolidus oxidation of Fe$^{3+}$ to Fe$^{2+}$ in Ilm$_a$ (Southwick 1968), which can be expressed as Fe$_2$O$_3$ · 5FeTiO$_3$ + 3Fe$_2$O$_3$ · Ti$_2$O$_3$ + 4TiO$_2$ · 3H$_2$O. The earlier exsolved rutile can act as a crystal seed and significantly lower the energy barrier needed for coarsening by absorbing Ti$^{4+}$ in the Ilm$_a$. The exsolved rutile also creates an interface with the Ilm$_a$. The lattice misfit ($\delta_{\text{Rt-Ilm}} = 6.9\%$) at the rutile-Ilm$_a$ interface may cause segregation of Fe$^{3+}$ from the Ilm$_a$ to the interface (Zhang and Zhang 2020), resulting in Fe$^{3+}$ enrichment at the interface. The Ti$^{4+}$ loss and Fe$^{3+}$ enrichment along the rutile-Ilm$_a$ interface facilitate the growth of anhedral magnetite along dendritic rutile (Fig. 5a). Therefore, the transformation of Ilm$_a$ to the magnetite-rutile symplectites stems from the exsolution of rutile in Ilm$_a$, which is intrinsically attributed to $f_{O_2}$ elevation during subsolidus cooling.
amphibole and biotite), Ilm$_a$ follows a steeply oxidizing $T$-$f_{O_2}$ trend, e.g., the cooling trend of KUIIB (Fig. 8), and transforms to the magnetite-rutile symplectite.

In this study, the bulk composition of the Ilm$_a$ for the investigated sample of the Xinjie intrusion is estimated to be Ilm$_{83}$Hem$_{15}$ (Table 2), and coexisting titanomagnetite is Us$_{90}$Mg$_{10}$ (Online Materials Table OM1). Our modeling results indicate that Ilm$_{83}$Hem$_{15}$ and Us$_{90}$Mg$_{10}$ can crystallize simultaneously at 952 °C and FMQ+0.51 (point “a” in Fig. 8). The Ilm$_{83}$Hem$_{15}$ may have experienced two-stage transformation along the subsolidus $T$-$f_{O_2}$ trends. Increasing $f_{O_2}$ of KUIIB would induce “oxy-exsolution” of Us$_{90}$$_{40}$Mg$_{55}$ at ~825 °C (point “b” in Fig. 8), and the oxidized Ilm$_{83}$Hem$_{15}$ at ~550 °C would form the rutile-magnetite symplectite (point “c” in Fig. 8) and Ti-rich solid solution of Ilm$_{92}$Hem$_{08}$. The Ilm$_{92}$Hem$_{08}$ is then decomposed into the ilmenite-hematite intergrowth on subsequent cooling (Fig. 8). This can well explain why the two intergrowths could occur into the ilmenite-hematite intergrowth on subsequent cooling (Fig. 8).

**Implications**

Magma hydration is the key to increase the $f_{O_2}$ of magma (Vekslar and Hou 2020) and to modify the crystallization sequence of evolved mafic magmas, triggering crystallization of extensive chromite and Fe-Ti oxide in layered intrusions (Reynolds 1985; Pang et al. 2008; Boudreau 2016; Vekslar and Hou 2020). This study reveals that the magnetite-rutile symplectite in Ilm$_a$ is essentially developed associated with the mineral assemblages crystallized from hydrated magmas. Therefore, the magnetite-rutile symplectite transformed from Ilm$_a$ can provide important clues of magma hydration, which is critical to understanding the subsolidus cooling history and related chromite-Fe-Ti oxide mineralization of layered intrusions elsewhere.

Water is also important to the evolution and crystallization of lunar and martian magmas (Gross et al. 2013; Hui et al. 2013; Filiberto et al. 2019). Although primary hydrous minerals in the lunar and martian rocks are direct evidence for hydrated magmas, they may be obscured by hydrothermal alteration, metamorphism, weathering, solar wind implantation, and meteorite impacts (Spandler et al. 2005; Sharp et al. 2013; Hui et al. 2013; Jolliff et al. 2019). On the other hand, ilmenite is ubiquitous in the martian and lunar rocks (Haggerty 1991; Wang et al. 2004; Santos et al. 2015) and is less susceptible to subsequent overprints. Primary textures that formed during crystallization and subsolidus cooling can be well preserved in ilmenite (e.g., Fig. 3). Therefore, magnetite-rutile symplectites may be an indicator of magma hydration in martian and lunar magmas even when other hydrous phases are no longer present.

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**FIGURE 8**. The diagram of Alog$_{f_{O_2}}$ (FMQ) vs. $T$ showing the isopleths of Fe-Ti oxide solid solution and the cooling trend of KUIIB buffer (biiite-ilmenite-feldspar-ulvöspinel) (modified after Frost 1991 and Harrison et al. 2000). Oxygen fugacity and temperature determined by QUILF-95 at $P=5$ kbar (Online Materials Table OM2). Us$_{10}$ refers to solid solution of ulvöspinel–magnetite$_{ss}$ (in molar fraction) and Ilm$_70$ refers to ilmenite–hematite$_{ss}$ and so on; Alog$_{f_{O_2}}$ refers to the FMQ buffer; “a” refers to the crystallization $T$-$f_{O_2}$ condition for Ilm$_{83}$Hem$_{15}$, coexisting Us$_{90}$Mg$_{10}$, “b” refers to the $T$-$f_{O_2}$ condition for “oxy-exsolution” of Us$_{90}$Mg$_{10}$, and “c” refers to the $T$-$f_{O_2}$ condition for transformation of Ilm$_{92}$Hem$_{08}$ to magnetite-rutile symplectite and ilmenite-hematite intergrowth.

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